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Composition and crystallization kinetics of R_2O–Al_2O_3–SiO_2 glass–ceramics

Dehua Xiong*, Jinshu Cheng, Hong Li

Key Laboratory of Silicate Materials Science and Engineering, Wuhan University of Technology, Ministry of Education, Wuhan 430070, China

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ABSTRACT

The crystallization behavior and microstructure of R_2O–Al_2O_3–SiO_2 (R means K, Na and Li) glass were investigated by means of differential scanning calorimeter (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystallization kinetic parameters including the crystallization apparent activation energy (E_a), the Avrami parameter (n), glass transition temperature (T_g) and the activity energy of glass transition (E_t) were also measured with different methods. The results have shown that: the DSC traces of composition A parent glass have two different precipitation crystallization peaks corresponding to E_{a1}(A) = 151.4 kJ/mol (Li_2SiO_3) and E_{a2}(A) = 623.1 kJ/mol ($Li_2Si_2O_5$), the average value of n = 1.70 ($Li_2Si_2O_5$) for the surface crystallization and E_t(A) = 202.8 kJ/mol. And E_a(B) = 50.7 kJ/mol (Li_2SiO_3), the average value of n = 3.89 (Li_2SiO_3) for the bulk crystallization and E_t (B) = 220.4 kJ/mol for the composition B parent glass. Because of the content of R_2O is bigger than composition A, composition B parent glass has a lower E_a, T_g and a larger n, E_t.

1. Introduction

Currently there has been a considerable amount of interest on crystallization behavior and other thermo-physical properties Li_2O–ZnO–SiO_2 glass–ceramics due to their beneficial properties, e.g., a wide range of thermal expansion coefficients (from 50 to $200 \times 10^{-7}/^{\circ}C$) by controlling heat treatments, high electrical resistivity and good chemical durability. These properties coupled with wide range of TEC make this glass–ceramics material suitable for fabrication of hermetic seals to a variety of metals and alloys including copper, stainless steel, etc. A number of studies on crystallization behaviors and other thermo-physical properties in Li_2O–ZnO–SiO_2 glass–ceramics system have been carried out [1–5]. The properties of glass–ceramics are dependant on the chemical composition and the thermal history. It is therefore important to gain a thorough understanding of the processes in the crystallization of the glass–ceramics. Study on crystallization kinetics of glass–ceramics to explore the effects of compositions on crystallization properties of glass, optimized the composition and improved the performance of glass–ceramics have important theoretical significance.

Isothermal and non-isothermal analysis methods have been used for collecting kinetic dates with the minimum of experimental measurements during the studies of glass crystallization kinetics for many years. Though DTA and DSC were proven techniques, the calculation results obtained from different methods are controversial over the use of these methods to study the parameters of crystallization kinetics [4]. The present investigation has monitored the crystallization kinetics of R_2O–Al_2O_3–SiO_2 (RAS) glass by using a variety of isothermal and non-isothermal analysis techniques. The crystallization behavior and microstructure of RAS glasses containing P_2O_5 were investigated by means of DSC, XRD and SEM. The crystallization kinetic parameters including the crystallization apparent activation energy (E_a), the Avrami parameter (n) and the activity energy of glass transition (E_t) were also measured with different methods.

2. Theoretical considerations

In non-isothermal transformation studies, the peaks crystallization exothermic temperature (T_p) on DSC traces of glasses were affected by the heating rate β. The crystalline phases have sufficient time to grow and T_p was low, the instantaneous rate of transformation is small and the crystallization peak flat when the heating rate β was slow. On the contrary, the glass crystallization lag phase transition and T_p increased, the instantaneous rate of transformation is great and sharp peak exothermic crystallization with a faster heating rate. According to the above exothermic crystallization characteristics and JMA equation, we can use differential methods of thermal analysis to study the glass to facilitate crystallization kinetics and calculate kinetic parameters of crystallization of glass.

Kinetics data, including activation energies (E_a) for crystallization, has also been derived employing non-isothermal techniques. The Avrami parameter (n) could be calculated by using isothermal analysis techniques. For example, from knowledge of the variation in peak crystallization temperature with heating rate, as originally

* Corresponding author. Tel.: +86 027 87860801; fax: +86 027 87860801.
E-mail address: xiongdehua@whut.edu.cn (D. Xiong).

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Table 1
The main chemical composition of parent glass (wt%).

Composition	$SiO_2 + Al_2O_3 + ZnO$	Li_2O	K_2O	Na_2O	P_2O_5	Sb_2O_3	R_2O/SiO_2
A	71.82	7.68	8.10	6.96	2.24	0.00	0.35
B	71.82	6.57	10.55	9.05	2.01	0.5	0.40

described by Kissinger [6,7]. Kissinger proposed that the activation energy of a first order process can be determined from the variation in peak temperature with heating rate using DSC from the relationship [4]:

$$\ln \frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + C_1 \quad (1)$$

In Kissinger equation, β is the heating rate, T_p is the peak temperature (e.g. crystallization peak temperature), and E_a is the activation energy, often described as an apparent activation energy. Plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ also is expected to be linear, and from the slop of the plot, the activation energy, E_a can be calculated.

The value of n can be attained from the following equation [8–10]:

$$\ln\ \Delta T = -\frac{nE_a}{RT_i} + C_3 \quad (2)$$

Here T_i is the random temperature in the DSC traces, ΔT is the vertical displacement from the baseline to the line of the crystallization exothermic peak at the temperature T_i. Plot of $\ln(\Delta T)$ versus $1/T_i$ also is expected to be linear, and from the slop of the plot is $-nE_a/R$, the Avrami parameter (n) can be calculated.

The relationship between the glass transition temperature T_g and the heating rate β can be discussed through the empirical equation:

$$T_g = A + B\ \ln \beta \quad (3)$$

where A and B are constants for a given glass composition [11,12]. Plot of T_g versus $\ln(\beta)$ for the prepared samples, the values of A and B can be obtained by using the least square fit, and this equation holds good for the studied samples. To obtain the activity energy of glass transition E_t, the data were fitted by the Kissinger method [7], which is most commonly used in analyzing crystallization data in DSC experiments. According to the Kissinger equation, the glass transition temperature T_g depends on the heating rate β as follows:

$$\ln \frac{\beta}{T_g^2} = -\frac{E_t}{RT_g} + C_4 \quad (4)$$

Based on the above relationship, plot of $\ln(\beta/T_g^2)$ versus $(1/T_g)$ for the prepared samples; slopes of these lines yield the values of E_t/R where E_t corresponds to the glass transition activation energy.

3. Experimental details

3.1. Preparation of parent glass

Based on our previous works [13–16], the composition of parent glass is shown in Table 1. All raw materials were chemical reagents with pure analysis; Sb_2O_3 was added as clarifier, P_2O_5 was used as compound nucleation agent. The reagents of SiO_2, Al_2O_3, Li_2CO_3, Na_2CO_3, K_2CO_3, ZnO, and $(NH_4)H_2PO_4$ were mixed and pulverized into powder in agate mortar, and then they were melted in the 200 ml alumina crucible at 1430–1460 °C for 3 h in an electric furnace. The melts were cast into the pre-heated graphite mold. Subsequently, the glass was annealed at 440–480 °C for 30 min and then cooled to room temperature in the furnace naturally. Finally, bulk transparent and parent glass without any bubbles were prepared.

3.2. Differential thermal analysis (DSC)

The parent glass were pulverized into powder (0.150–0.075 mm) suitable for DSC employing a NETZSCH (STA 449C) DSC with the temperature range of 20–1000 °C. The glass powder with the weight of 30 mg was contained in a platinum crucible and the reference material was α-Al_2O_3 powders. The data were recorded by means of a chart recorder. The samples were heated in air from ambient temperature to 1000 °C at heating rates of 5, 10, 15 and 20 °C/min.

3.3. X-ray diffraction (XRD)

The glass–ceramics were pulverized into powder in agate mortar and subjected to pass 200 meshes sieve for XRD analysis. The types of crystal phases after heat treatment were analyzed by XRD (Rigaku D/max-RA) using copper Kα radiation, produced at 35 kV and 30 mA, with 2θ = 10–60°and 0.02° per second, and the diffraction patterns were analyzed by the use of MDI Jade 5.0 software.

3.4. Scanning electron microscope (SEM)

For SEM (JSM-5610V) observation, the specimens which were polished by diamond slurry and chemically etched by 4 volume hydrofluoric acid for 30 s were used. The microstructures of crystal phases could be observed in this way.

4. Results and discussion

Typical DSC traces of two similar glass compositions crystallized at heating rates of 5, 10, 15 and 20 °C min^{-1} are shown in Figs. 1 and 2. The thermal parameters are summarized in Table 2, where T_g is the glass transition temperature (extrapolated onset), T_{p1} and T_{p2} are the first and second crystallization peak temperatures, respectively.

The endothermic base line shift at 425-460 °C (Fig. 1) indicates the glass transition temperature in case of composition A parent glass system and the sharp exothermic peaks at the onset values of 620–675 and 820–875 °C are two crystallization temperatures

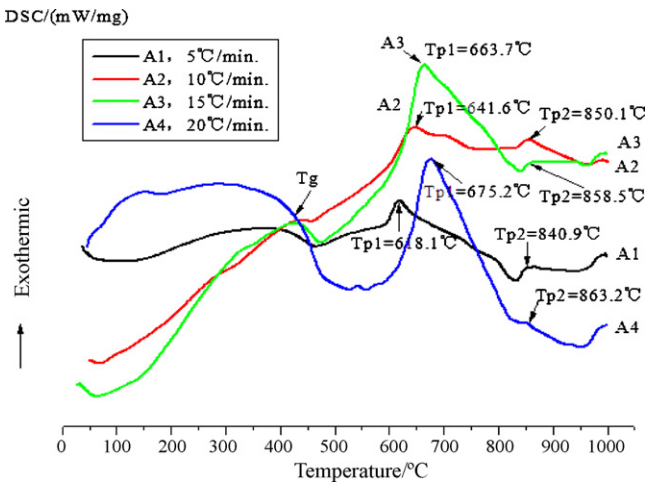

Fig. 1. DSC traces of the composition A glass.